

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 33/14, 33/26, C02F 1/56	A1	(11) International Publication Number: WO 98/31748 (43) International Publication Date: 23 July 1998 (23.07.98)
(21) International Application Number: PCT/GB98/00161 (22) International Filing Date: 19 January 1998 (19.01.98) (30) Priority Data: 9701090.4 20 January 1997 (20.01.97) GB 9726677.9 17 December 1997 (17.12.97) GB (71) Applicant (for all designated States except US): ALLIED COLLOIDS LIMITED [GB/GB]; P.O. Box 38, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): GHAFPOOR, Mark, Sir-faraz [GB/GB]; 9 Moorgate Avenue, Fagley, Bradford, West Yorkshire BD3 7LR (GB). SKINNER, Malcolm [GB/GB]; 82 Bolton Lane, Bradford, West Yorkshire BD2 4BA (GB). JOHNSON, Ian, Michael [GB/GB]; 23 Bankfield Drive, Nab Wood, Shipley, West Yorkshire BD18 4AD (GB). (74) Agent: GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: AQUEOUS DISPERSION OF CATIONIC POLYMER AND ITS PRODUCTION AND USE (57) Abstract A stable, pourable, liquid composition contains a blend of at least 8 % (usually at least 15 %) water soluble high IV cationic polymer and a water soluble low IV cationic coagulant polymer which preferably comprises polyamine, and water soluble inorganic salt.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NI	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroun	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

AQUEOUS DISPERSION OF CATIONIC POLYMER AND ITS PRODUCTION AND USE

This invention relates to fluid, polymeric, compositions which contain both a high IV cationic polymer and a low IV cationic coagulant polymer, their production and their use.

It is well known to supply and use water soluble, high cationic charge, low IV (intrinsic viscosity) coagulant polymers. Often they are supplied to the customer in the form of aqueous solutions. Although the fact that these materials have relatively low IV and low molecular weight is sometimes an advantage, there are many occasions when it would be desirable if they could additionally perform in a manner that would be more usually associated with higher molecular weight materials.

Higher molecular weight, water soluble, polymers (generally of lower ionic charge) are frequently used as flocculants. Because of their higher IV and molecular weight, it is usually impracticable to supply them as aqueous solutions containing more than, at the most, 5 or 10% by weight polymer since even at 5% concentration the solutions are liable to have high viscosity, and they may even be a rigid gel at higher concentrations. Accordingly flocculant polymers are generally supplied to the customer as powders or as reverse phase emulsions (including dispersions) in oil.

When the customer receives a powder, it is generally necessary for the customer to dissolve that powder in water prior to use, and the dissolution process can be slow and inconvenient. When the customer receives an emulsion, it is again generally necessary to dissolve the polymer of the emulsion into water during use and the resultant solution is contaminated with surfactant and the oil or other continuous phase of the emulsion. This is undesirable.

There have therefore been numerous attempts to provide water soluble, relatively high molecular weight, polymer in an aqueous composition (thereby avoiding the disadvantages

of dissolving powder or dealing with the oil continuous phase) wherein the resultant composition has acceptable viscosity but much higher concentration than would be associated with that high molecular weight polymer if dissolved in water.

These attempts involve suppressing swelling and/or dissolution of the higher molecular weight polymer by modification of the aqueous continuous phase in which it is dispersed and/or by modification of the polymer. Such products are generally referred to as "water-in-water emulsions", even though the physical state of the higher molecular weight material may not necessarily be a true emulsion.

An early disclosure of a water-in-water emulsion is in U.S. 4,389,600. This describes polymerising monomers in an aqueous phase containing a water soluble polymer. Inorganic salt can be added before or after the polymerisation. Thus, in Example 21, acrylic acid is polymerised in a solution of 100g water, 15g PEG, 10g polyvinyl alcohol and 15g NaCl. Although the generic description includes both non-ionic and ionic water soluble polymers for the solution, the polymer which is used as the sole or main polymer in the solution in most of the examples is a polyethylene glycol, for instance having molecular weight which can range from 6,000 to 20,000.

The only named ionic material is polyethylene imine and, in the examples, when this is used it is used solely as a minor component with a much larger amount of non-ionic polymer. It is necessary that the solution viscosity should not be too high (as otherwise the composition is not pourable) and this places severe constraints on the monomers which can be polymerised in the aqueous phase and the IV or molecular weight to which they can be polymerised.

Although U.S. 4,380,600 alleges that the described technique using polyethylene glycol is capable of giving fluid dispersions of high molecular weight polymer, so far

as we are aware this process has not proved commercially successful. A reason for this may be that evidence by others has indicated to us that reproduction of an example in it did not lead to a fluid composition but instead led to something which became solid quite quickly. Hydroxy compounds are mentioned in JP 6136225, EP-A-183,466 and EP-A-630,909.

In EP 169,674 we describe the formation of fluid compositions by milling preformed, high molecular weight, polymer gel of, for instance, cationic polyacrylamide into a continuous phase of, for instance, low molecular weight polymeric DADMAC (diallyl dimethyl ammonium chloride) or polyamine or polyethylene imine. However this necessitated the preliminary formation of aqueous polymer gel and its incorporation into the continuous phase, and it was difficult to obtain a fluid composition that had good storage stability and low viscosity at relatively high polymer content.

Processes are known in which the tendency of the higher molecular weight polymer to swell and dissolve into the aqueous phase is suppressed by copolymerising into that polymer a relatively hydrophobic monomer (for instance U.S. 5,403,883, 5,614,602 and 5,480,934 and EP-A-525,751). In other processes various additives are included in the aqueous phase in order to try to control swelling and dissolution of the polymer, for instance polymeric dispersant in CA 2,143,564 and 2,140,817 and polyvalent salt in U.S. 4,929,655 and 5,006,590. Hydrophobic polymeric dispersant is proposed in U.S. 5,597,859 and CA-A-2,125,545. However it seems none of these proposals have been widely adopted commercially and the need remains to try to find a satisfactory way of providing an aqueous composition which has adequately low viscosity and yet which contains both coagulant and flocculant in usefully high concentrations and wherein the flocculant can have a usefully high molecular weight.

In EP 262,945 we described forming a cationic polymer by polymerisation within an aqueous phase of, for instance, aqueous polyamine or aqueous poly DADMAC. In the examples, cationic homopolymer was formed. In example 1, a composition was formed of about 12% cationic homopolymer, 12% polyamine and 76% water and the viscosity of the composition was rather low. In another example 2 the composition was formed of about 16% cationic homopolymer, 16% poly DADMAC and 67% water. The viscosity was higher.

It would be desirable to be able to provide a fluid, pourable, stable composition which has a relatively high content of active polymer (e.g., active for the purposes of coagulation or flocculation) and which is in the form of a water-in-water emulsion. It would be desirable to provide such a dispersion having a high content of high IV polymer, and to provide flocculation processes using such compositions.

According to the invention we provide a stable, pourable, liquid composition containing 15 or 20 to 60% by weight of a blend of a water soluble high IV cationic polymer and a water soluble low IV cationic coagulant polymer,

wherein the water soluble high IV polymer is a polymer of water soluble ethylenically unsaturated monomer or monomer blend which includes cationic monomer and the polymer has an apparent IV (defined below) of at least 2dl/g and is present in a composition in an amount of at least 8% by weight, preferably above 15% by weight,

the water soluble low IV cationic coagulant has an IV (defined below) of not more than 1.5 dl/g and preferably comprises a polyamine which is present in an amount of less than 25%,

and the composition has a viscosity (Brookfield RVT, spindle 6, 20rpm, 25°C) of less than 30,000cps and is a dispersion of the high IV polymer in an aqueous phase which is an aqueous solution of the low IV coagulant polymer and water soluble inorganic salt.

Thus the invention provides an aqueous, oil-free, fluid composition of high IV polymer and which is fluid despite having a high polymer content.

The pourable composition is made by forming the aqueous phase which is the aqueous solution of the coagulant polymer and the inorganic salt, dissolving the monomer or monomer blend which is to provide the high IV polymer in that aqueous phase and then polymerising the monomer or monomer blend to form the high IV polymer dispersed in the aqueous phase.

The composition is stable, pourable and liquid in the sense that substantially no permanent settling occurs when the composition is allowed to stand for several weeks and the composition has a sufficiently low viscosity that it can be poured. Preferably no sedimentation occurs, but if any sedimentation does occur the sedimented phase is capable of being re-suspended by simple stirring. The viscosity of the composition is preferably below 20,000cps, most preferably below 15,000cps and often below 10,000cps. It can be as low as, for instance, 500 or 1,000cps but is generally above 2,000cps. All these values are determined by Brookfield RVT, spindle 6, 20 rpm. The polymers also have a viscosity in the range 1,000 to 25,000cps or 30,000cps when measured at 10 rpm.

The composition preferably has the form of a clear liquid or an opaque liquid. It is substantially free of gel or lumps. If such gel or lumps form then it is necessary to modify the aqueous phase so as to achieve the desired pourable liquid state. For instance the amount of coagulant polymer or inorganic salt may be varied.

The monomers of which the high IV polymer are formed may consist solely of cationic monomer so that the polymer can be a cationic homopolymer or a copolymer made from two or more different cationic monomers. Often, the monomers are a blend of one or more cationic ethylenically unsaturated monomers with one or more other ethylenically unsaturated monomers. Thus the polymer may be formed from

1 to 100% by weight cationic monomer and 0-99% other monomer. Often the blend is formed with acrylamide or other water soluble ethylenically unsaturated non-ionic monomer. The polymer may be a cationic amphoteric polymer, in which event ethylenically unsaturated anionic monomer is included in the monomer blend in an amount which is not more than the amount of cationic so as to give a cationic amphoteric polymer. The anionic monomer may be a carboxylic monomer or a sulphonic monomer, e.g., acrylic acid or AMPS.

Preferred polymers contain at least 10% and usually at least 30% and often at least 50% (by weight of the total monomer) of the chosen cationic monomer or monomers. If acrylamide or other non-ionic or anionic monomer is present, the amount is usually at least 0.5% by weight, e.g., 10 to 70%. If anionic monomer is included, the amount of anionic monomer is below 50% and usually 0.5 to 25% by weight, but often it is zero.

The cationic monomer can be a diallyl quaternary monomer, generally diallyl dimethyl ammonium chloride DADMAC, but preferably is a dialkylaminoalkyl (meth) -acrylate or -acrylamide, wherein the alkyl groups generally contain 1 to 4 carbon atoms. Examples are dimethyl or diethyl aminoethyl or propyl (meth) -acrylate or -acrylamide or dimethyl or diethyl aminomethyl (meth) acrylamide. The monomer may be introduced as an acid addition salt or quaternary ammonium salt or the polymer may be converted into such a salt after polymerisation. The quaternising group is usually methyl chloride or other aliphatic quaternising group. Preferably the high IV polymer is substantially free of hydrophobic, solubility-reducing, groups such as C4 or higher alkyl (e.g., above C8) or aromatic (such as benzyl) groups on the quaternary nitrogen or elsewhere, since such materials are unnecessary in the invention and reduce the cost performance benefit of the products.

The high IV cationic polymer can be made in the presence of a small amount (typically 5 to 1,000ppm, often 5-100ppm) of polyethylenically unsaturated monomer or other cross linking agent so as to give products which have an ionic regain of at least 20%, as described in EP 202,780.

The high IV polymer is formed by polymerisation in the composition under conditions such that it has an apparent IV of at least 2dl/g and usually considerably more. For instance usually it has an apparent IV of at least 4dl/g and thus its molecular weight is sufficiently high that it will contribute useful bridging flocculation properties when used for treating a suspension. The apparent IV is often above 5dl/g up to 14dl/g or higher. Generally it is in the range 5 to 12dl/g.

All these values are the apparent IV, that is to say the intrinsic viscosity as determined by observation of viscosities of aqueous compositions prepared from the whole composition of the invention in one molar sodium chloride buffered to pH 7.5 at 25°C using a suspended level viscometer, wherein the apparent IV is determined by calculation based on the weight of the high IV polymer in the composition. Thus if, for instance, the composition contains 10% by weight of the acrylamide polymer the entire composition is utilised for preparing the solution required for IV measurements but the amount of polymer in such solutions, when calculating the IV, is assumed to be 10% by weight of the composition. The IV measured at pH 7.0 will be close to the IV measured at pH 7.5 and pH 7.0 can be used instead of pH 7.5.

The amount of the water soluble high IV cationic polymer is usually above 15% and preferably it is at least 17% and generally at least 20%. Preferred compositions generally contain from 20 or 25% up to 30 or 35%, but compositions of the invention can contain as much as 40% of the high IV polymer or more. These percentages are by weight of the total composition.

The water soluble low IV cationic coagulant has an IV of not more than 1.5 dl/g as measured using a suspended level viscometer on solutions of the coagulant polymer alone in 1 molar sodium chloride buffered to pH 7.5 at 25°C. It is generally present in an amount of at least 2 or 3%, often at least 5%, by weight of the composition. The cationic coagulant preferably comprises a polyamine coagulant polymer, for instance a polymer made by condensation of an amine and/or a diamine or higher amine (e.g., ethylene diamine or tetraethylene pentamine) with epichlorohydrin or other epihalohydrin or with dichloroethane or other dihalo alkane. Preferred polymers are formed by condensation of epichlorohydrin with dimethylamine and a small amount of ethylene diamine or other multi-amine to cause cross linking.

Usually the polyamine coagulant is used as the only low IV cationic coagulant but if desired blends of it with other low IV cationic coagulants can be used. If a blend of coagulant polymers is being used, the polyamine is usually more than 50% (and generally above 80%) of the blend. The total amount of polyamine (and usually the total amount of low IV cationic coagulant) is less than 25% but is usually at least 2 or 3% by weight of the total composition. Generally it is not more than 15% and preferably not more than 10%.

One suitable other cationic coagulant that can be used as part of the coagulant polymer is cationic dicyandiamide polymer. Another suitable coagulant polymer is polyethyleneimine. Another is a homopolymer or a high cationic copolymer of water soluble ethylenically unsaturated cationic monomer optionally with a comonomer, usually not more than 30% by weight acrylamide. The cationic monomer can be any of those discussed above for the high IV polymer but is preferably DADMAC.

Although it is not preferred (since the resultant compositions normally have to include less of the high IV

polymer) the polyamine can also be replaced entirely by one or more of these coagulant polymers.

The only essential polymers which are present in the invention are preferably conventional water soluble high IV
5 and water soluble low IV polymers. Thus, in the invention, it is preferred that there is no deliberate addition of a polymer which contains hydrophobic groups and which will therefore have a significantly lower solubility in water than conventional water soluble coagulant and flocculant
10 polymers.

When referring to a water soluble monomer we mean that the monomer has conventional high solubility at 25°C, generally above 5 or 10% in deionised water, and similarly a water soluble polymer has conventional high water
15 solubility typically of above 5 or 10% in deionised water, at which concentration it may form a gel when the IV is high.

Compositions of the invention preferably contain more of the high IV polymer than the coagulant polymer, e.g., a
20 weight ratio of 1:0.1 to 1 and generally 1:below 1, usually around 1:0.15 to 0.5.

The amount of water in the composition is usually from 30 to 70%, preferably around 40 to 60%, and in particular it is generally in the range 45 to 55% by weight of the
25 total composition.

It is necessary to include water soluble inorganic salt in the composition. The amount is normally at least 10% by weight and is usually at least 15% by weight of the composition. It can be as much as 30% or even 35%. The
30 upper limit is dictated primarily by the solubility of the particular salt in the composition, and in particular in the aqueous phase of the composition, since it is unnecessary and therefore undesirable to have significant amounts of undissolved salt in the composition. Preferably
35 substantially all the salt is in solution. Preferably the concentration of salt is substantially the saturation concentration of that salt in the composition, for instance

being an amount of 80 to 105%, preferably 90 to 100%, of the saturation concentration.

The salt is preferably a salt which has high solubility in water and it can be an ammonium, alkali metal or alkaline earth metal chloride, bromide or iodide, such as ammonium chloride, sodium chloride or magnesium chloride, or it can be a sulphate such as ammonium sulphate. Water soluble polyvalent salts, such as polyaluminium chloride, can be used and have the advantage that their presence may then contribute to the performance of the composition since such polyvalent salts often have coagulating properties themselves. Mixtures of salts are often preferred, especially ammonium sulphate and sodium chloride.

The composition is generally made by dissolving most or all of the salt in an aqueous solution of the polyamine (optionally blended with other polymeric coagulant) preferably so as to provide a solution which is substantially saturated in the salt, and then adding the monomer or monomer blend. Often it is desirable for the monomer or monomer blend to be added as an aqueous solution and it is then generally preferred for this solution to contain inorganic salt, preferably in an amount such that the solution is substantially saturated in the salt. Polymerisation of the monomer or monomer blend in the aqueous phase can be initiated using thermal initiator or redox initiator. Initiator may be added both to start the reaction and during the reaction. It is added in an amount and at a time which will result in the polymer having the chosen IV.

If desired, polyethylene glycol or other multi-hydroxy compound may be included in the coagulant solution, in order to promote stability and reduce viscosity but this is usually unnecessary. The multi-hydroxy compound can be a dihydroxy, trihydroxy or higher hydroxy compound such as glycerol or a polymer such as polyvinyl alcohol. When polyethylene glycol is being used the molecular weight is

preferably below 1000, e.g., about 200, but can be higher e.g., up to 4000 or even 10000.

The compositions of the invention can be used either by direct addition to a suspension which is to be treated or, more usually, after dilution to a total concentration of high IV and cationic coagulant, of generally less than 10% and frequently 0.1 to 5% by weight.

The suspension which is to be treated can be any suspension which can advantageously be treated by the two polymers either individually or in combination. Thus it may be a cellulosic suspension, for instance a paper making suspension wherein the composition is used as retention or drainage aid, or it may be a cellulosic, municipal or industrial waste suspension, especially sludges.

In the following examples, all weights are for 100% active components.

DMAEA q MeCl = Dimethylaminoethyl acrylate quaternised with MeCl

DMAEMA q MeCl = Dimethylaminoethyl methacrylate quaternised with MeCl

ACM = Acrylamide

Na AMPS = Sodium salt of 2-acrylamido 2-methyl propane sulphonic acid

TAAC = Tetraallyl ammonium chloride

APTAC = Acrylamido trimethyl ammonium chloride

Example 1

Preparation of a water in water emulsion product, in which the flocculant has an ionic charge of 60% (weight) and the coagulant:flocculant ratio is 0.2:1.

Into a 1 litre flask fitted with a stirrer, condenser, nitrogen and thermometer was charged the continuous phase comprising

water	145.2g
polyamine	30.9g
ammonium sulphate	82.8g

The continuous phase was purged with nitrogen for one hour.

A monomer phase was prepared from

DMAEA q MeCl	92.8g
ACM	54.1g
Adipic acid	7.6
5 water	96.2g
NaCl	13.1g

The monomer phase was added to the continuous phase.
The following initiators were then added

1.42mls of 10% 2,2 azobis (2-amidopropane
10 hydrochloride)

2.14mls of 0.5% ammonium persulphate

2.14mls of 0.5% potassium bromate

2.14mls of 1.0% sodium sulphite

The reaction is allowed to exotherm followed by
15 leaving the reaction at 70°C for a further hour.

The resulting product has a concentration (dry weight)
of 53.8% and a Brookfield viscosity of 11400cps.

The apparent IV of the high IV polymer is 6.1dl/g.

The active content is 36% polymer, with the content of
20 high IV polymer being 30%.

Example 2

Preparation of a water in water emulsion product in
which the flocculant component has a cationic charge of 40%
and the coagulant flocculant ratio is 0.4:1.

25 As for example 1 with the continuous phase being
polyamine

polyamine	61.7g
ammonium sulphate	141.7g
water	195.4g

The monomer phase being

30 ACM	148g
DMAEA q MeCl	98.6g
Adipic acid	7.7g
NaCl	16.91g
water	104.4g

35 Initiators were as in example 1.

The resulting composition had a viscosity of 8,500cps.

The active content is 46.5% polymer, with the content of high IV polymer being 32.8%.

Example 3

Preparation of a water in water emulsion product in which the flocculant component has a cationic charge of 60% and the coagulant:flocculant ratio is 0.2:1.

Continuous phase comprising

water	145.2g
polyamine	30.9g
ammonium sulphate	82.8g

The continuous phase was purged from nitrogen for one hour.

A monomer phase was prepared from

DMAEA q MeCl	92.8g
ACM	54.1g
Adipic acid	7.6
water	96.2g
NaCl	13.1g
4.3mls of 1% TAAC	

The monomer phase was added to the continuous phase. Initiators as for example 1.

The reaction is allowed to exotherm followed by leaving the reaction at 70°C for a further hour.

The resulting product has a concentration (dry weight) of 53.1% and a Brookfield viscosity of 7500cps.

The apparent IV of the high IV polymer was not measured as the any prepared solutions were highly structured and showed an ionic regain (see EP-A-202,780) of 26% after shearing.

The active content is 36% polymer, with the content of high IV polymer being 30%.

Example 4

Preparation of a water in water emulsion product in which the flocculant has a cationic charge of 100% (wt) - using APTAC.

The coagulant to flocculant ratio of 0.5:1.

Into a 1 L flask fitted with stirrer, condenser, nitrogen purge and thermometer was charged the continuous phase

	polyamine	55.0g
5	$(\text{NH}_4)_2\text{SO}_4$	161.7g
	water	199.3

The continuous phase was then degassed with nitrogen for 30 minutes.

	A monomer phase was prepared from	
10	APTAC	110g
	H ₂ O	24g

The monomer was then added to the continuous phase and allowed to disperse for 5 minutes.

1.42mls azo-initiator as in Example 1 were added before the reaction was warmed to 50°C and allowed to exotherm.

The reaction temperature was then maintained at 70°C for a further hour.

The resulting product has a concentration (dry weight) of 59.4% a Brookfield viscosity of 18,200cps.

The apparent IV of the high IV polymer is 4.9dl/g.

The active content is 30% polymer, with the content of high IV polymer being 20%.

Example 5

25 Preparation of a water in water emulsion product in which the flocculant has a cationic charge of 60% (wt) - using APTAC.

The coagulant to flocculant ratio is 0.2:1.

30 Into a 1 L flask fitted with stirrer, condenser, nitrogen purge and thermometer was charged the continuous phase

	polyamine	30.9g
	$(\text{NH}_4)_2\text{SO}_4$	89.2g
	water	123.1g

35 The continuous phase was then degassed with nitrogen for 30 minutes.

A monomer phase was prepared from

15

	ACM	54.1g
	APTAC	92.9g
	Adipic Acid	7.7g
	NaCl	18.1g
5	H ₂ O	98.0g

The monomer was then added to the continuous phase and allowed to disperse for 5 minutes. 1.42mls azo-initiator was added as in Example 1 before the reaction was warmed to 50°C and allowed to exotherm.

10 The reaction temperature was then maintained at 70°C for a further hour.

The resulting product has a concentration (dry weight) of 57% and a Brookfield viscosity of 12,500cps.

The apparent IV of the high IV polymer is 5.4dl/g.

15 The active content is 36% polymer, with the content of high IV polymer being 30%.

Example 6

Preparation of a water in water emulsion product in which the flocculant has a cationic charge of 20% (wt).

20 The coagulant to flocculant ratio is 0.2:1.

Into a 1 L flask fitted with stirrer, condenser, nitrogen purge and thermometer was charged the continuous phase

	polyamine	23.8g
25	(NH ₄) ₂ SO ₄	119.6g
	water	165.2g

The continuous phase was then degassed with nitrogen for 30 minutes.

	ACM	89.1g
30	DMAEMA.gMeCl	23.8g
	Adipic Acid	5.9g
	NaCl	16.4g
	H ₂ O	106.2g

35 The monomer was then added to the continuous phase and allowed to disperse for 5 minutes. 1.42mls azo-initiator were added as in Example 1 before the reaction was warmed to 50°C and allowed to exotherm.

The reaction temperature was then maintained at 70°C for a further hour.

The resulting product has a concentration (dry weight) of 50.6% and a Brookfield viscosity of 9200cps.

5 The IV of the flocculant polymer is 7.1dl/g.

The active content is 25.9% polymer, with the content of high IV polymer being 21.6%.

Example 7

10 Preparation of a water in water emulsion product, in which the flocculant has an ionic charge of 55% Cationic, 10% anionic (weight) and the coagulant:flocculant ratio is 0.46:1.

15 Into a 2 litre flask fitted with a stirrer, condenser, nitrogen and thermometer was charged the continuous phase comprising

water	310g
polyamine	99.6g
ammonium sulphate	176g

20 The continuous phase was purged with nitrogen for one hour.

A monomer phase was prepared from

DMAEA q MeCl	118.1g
ACM	64.4g
Adipic Acid	10.7g
25 water	96.2g
NaAMPS	21.5g

The monomer phase was added to the continuous phase.

The following initiators were then added.

2.0mls of azo-initiator of Example 1

30 1.5mls of 1% ammonium persulphate

1.5mls of 1% potassium bromate

2.0mls of 2% sodium sulphite

The reaction is allowed to exotherm followed by leaving the reaction at 70°C for a further hour.

35 The resulting product has a concentration (dry weight) of 54.6% and a Brookfield viscosity of 11,400cps.

The apparent IV of the high IV polymer is 6.8dl/g.

The active content is 35% polymer, with the content of high IV polymer being 23.9%.

Example 8

Preparation of a water in water emulsion in which the
5 flocculant has a cationic charge of 60% and the coagulant
flocculant ratio is 0.3:1.

The process is conducted broadly as in Example 1,
using the initiators of Example 1. The continuous phase is

	polyamine	37.7g
10	PEG 200	20g
	Ammonium Sulphate	75.8g
	Sodium Chloride	15g
	Water	142.3g

The monomer phase is

15	ACM	43.9g
	DMAEAq MeCl	75.3g
	Adipic Acid	6.3g
	Water	103.7g

The resulting product has a concentration (dry weight)
20 of 50.8% and a Brookfield viscosity of 5000cps.

The high IV, flocculant, polymer has an apparent IV of
7.8dl/g and its concentration in the product is 25.1%.

CLAIMS

1. A stable, pourable, liquid composition containing 15 to 60% by weight of a blend of water soluble high IV cationic polymer and a water soluble low IV cationic
5 coagulant polymer wherein
the water soluble high IV cationic polymer is formed of a water soluble ethylenically unsaturated monomer or monomer blend which includes cationic monomer and the polymer has an apparent IV of at least 2dl/g and is present
10 in the composition in an amount of at least 8% by weight,
the water soluble low IV cationic coagulant has an IV of below 1.5dl/g present in an amount of below 25% by weight,
and the composition has a Brookfield viscosity of less
15 than 30,000cps and is a dispersion of the high IV polymer in an aqueous phase which is an aqueous solution of the low IV coagulant polymer and water soluble inorganic salt.
2. A composition according to claim 1 in which the amount of salt is substantially the saturation concentration of
20 salt in the aqueous solution.
3. A composition according to claim 1 or claim 2 in which the ratio by weight of high IV polymer to coagulant polymer is from 1:0.1 to 1:1.
4. A composition according to claim 3 in which the ratio
25 is 1:0.15 to 1:0.5.
5. A composition according to any preceding claim in which the amount of high IV polymer is above 15%.
6. A composition according to any preceding claim in which the amount of high IV polymer is 17 to 35%.
- 30 7. A composition according to any preceding claim in which the high IV polymer is formed from 1 to 100% ethylenically unsaturated cationic monomer and 0 to 99% other ethylenically unsaturated monomer selected from anionic monomers in an amount less than the amount of
35 cationic monomer and non-ionic monomers.

8. A composition according to claim 7 in which the high IV polymer is formed of 20 to 90% cationic monomer and 10 to 80% acrylamide.
9. A composition according to claim 7 or claim 8 in which
5 the cationic monomer is a dialkylaminoalkyl (meth) - acrylate or -acrylamide as acid addition or quaternary ammonium salt or is diallyl dimethyl ammonium chloride.
10. A composition according to any preceding claim in which the low IV cationic coagulant comprises polyamine.
- 10 11. A composition according to any preceding claim in which the low IV cationic coagulant comprises polyamine in an amount of 3 to 15%.
12. A composition according to any preceding claim in which the composition is free of polymers containing
15 hydrophobic groups which include alkyl containing 4 or more carbon atoms or aryl.
13. A process of making a composition according to any preceding claim comprising dissolving the monomer or monomers which are to be polymerised to form the high IV
20 polymer in an aqueous solution of the coagulant polymer and the inorganic salt in an amount sufficient substantially to saturate the solution, and polymerising the monomer or monomers.
14. A process of flocculating and/or coagulating a
25 suspension comprising dosing into the suspension a composition according to any of claims 1 to 12 or a dilute aqueous solution formed by diluting with water a composition according to any of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 98/00161

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L33/14 C08L33/26 C02F1/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C02F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 717 056 A (HYMO CORP) 19 June 1996 see examples 6-9 ---	1-8, 13, 14
X	EP 0 637 598 A (NALCO CHEMICAL CO) 8 February 1995 see example 7 -----	1-9, 13, 14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

14 April 1998

Date of mailing of the international search report

29/04/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rodriguez, L

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/00161

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0717056 A	19-06-96	AU 4047295 A	20-06-96
		CA 2165385 A	16-06-96
		CN 1133302 A	16-10-96
		JP 8225621 A	03-09-96
		SG 33629 A	18-10-96
		US 5708071 A	13-01-98
EP 0637598 A	08-02-95	CA 2125545 A	11-12-94
		CN 1100434 A	22-03-95
		DE 69402924 D	05-06-97
		DE 69402924 T	02-01-98
		JP 7053640 A	28-02-95
		US 5597858 A	28-01-97